Absorption of Sparingly Soluble Gases by Reactive Media in Self-Aerated Gas-Liquid Contactors: a Scale-up Procedure

Yury Zundelevich

January 1995

Lawrence
Livermore
National
Laboratory

Absorption of Sparingly Soluble Gases by Reactive Media in Self-Aerated Gas-Liquid Contactors: a Scale-up Procedure

Yury Zundelevich

Introduction

Absorption of sparingly soluble gases, such as NO or O_2, is greatly enhanced and, indeed, made possible if the latter react with the media. Among a dozen of reactive solvents for NO_x abatement reviewed by Jethani et al. (1990) [1] aqueous acidic urea appears the most economically and environmentally attractive because urea is a cheap reagent and because products of reaction of urea with nitrous acid, formed in the liquid phase via absorption of NO and NO_2, are carbon dioxide and nitrogen, which can be directly released into the atmosphere. That makes urea process unique among other wet scrubbing processes that routinely produce secondary waste. The urea process has been patented by Warshaw (1971) in the USA and by Dyens (1985) in France but its full potential has never been realized, perhaps due to the lack of an *efficient gas-liquid contactor* to overcome low solubility of NO in aqueous solutions.

In conjunction with the electrochemical destruction of organics (MEO) in waste streams, LLNL has recently designed and built a bench scale gas-liquid contactor for nitric acid regeneration with oxygen. The contactor proved very effective in overcoming the problem of low solubility of oxygen converting back to nitric acid approximately 99% of nitrous acid formed at the cathode (which would otherwise convert to NO_x). The history of the contactor goes back to the seventies when it was developed by Zundelevich (1975, 1979) [3-4] for oxidative pressure leaching with oxygen in the former Soviet Union. The bench scale contactor consists of a 12" diameter tank with self-inducting impeller/aerator of very high gas capacity. The aerator represents a 3.5" turbine mounted on a vertical shaft inside the draft tube equipped with a stator. During operation the lower half of the turbine induces liquid and the upper half induces gas from the draft tube. Fine gas-liquid dispersion with large mass transfer area is formed within the high shear rate zone of rotor-stator assembly yielding mass transfer rates unattainable in conventional packed absorbers. Once the gas, in the form of bubbles, reaches the surface it is drawn again into the draft tube (and thus given another chance to pass through the liquid), the off-gas circulation rate being many times its overall throughput across the contactor.

The new contactor offers two approaches to solving the NO_x pollution problem. Where full recovery of nitric acid is desired, oxygen can be fed into the contactor to convert nitrous acid into nitric. This approach was demonstrated at LLNL. Alternately, in the proposed acidic urea process nitrous acid, as it forms from NO_x, would be converted to nitrogen, water and carbon dioxide.

Feasibility of common scale-up procedure for acidic urea and nitrous acid oxidation processes

The acidic urea process chemistry is completely different from that of nitrous acid oxidation and since the only bench scale gas-liquid contactor became an integral part of the present MEO system, another one would be required to obtain the data necessary for the urea process scale-up. However, there is strong evidence that the acidic urea $DeNO_X$ scale-up should be no different from that for the nitrous acid conversion.

In general, when gas absorption process is accompanied by fast chemical reactions in liquid phase (they are usually fast or can be made fast by raising the temperature), the mass transfer becomes rate limiting and thus a basis for scale-up. A direct proof that the chemical reaction is fast with respect to the mass transfer, would be to show that the actual concentration C of the gaseous reactant in the liquid phase is much lower than the equilibrium concentration C^* predicted from the Henry's law. That would indicate that the gaseous reactant (e.g., oxygen for MEO) is consumed as soon as it is delivered. The dissolved oxygen concentration wasn't measured in the MEO experiments, but some relevant observations have been made. Whenever oxygen supply to the contactor was interrupted, nitrous acid in the catholyte would build-up and decompose releasing NO_X. The NO_X was vented from the contactor via hose into the glass filled with water and formed increasingly strong jet hitting the bottom of the glass. Each opening of oxygen valve at that point would *instantaneously* reduce the jet strength or annihilate it completely. Such an immediate control would not be possible if the nitrous acid oxidation rate (or oxygen consumption) lagged behind the oxygen dissolution rate (delivery) and indicated that oxygen was consumed instantly. The observation is also consistent with Fig. 1 where the measured conversion efficiency is plotted as function of the product of the rotor tip speed and the gas circulation factor, the parameters directly affecting the oxygen transfer rather then the reaction rate. Strong effect of mass transfer (and thus, the mass transfer control) is seen to extend up to 98% conversion. Only then the response to oxygen delivery weakens as the reaction in liquid phase essentially depleted of nitrous acid at that point slows enough to eventually take over as the rate controlling factor.

Similarly, regarding the acidic urea process, there is a sufficient body of evidence (cf. Warshaw, 1971) in the literature that absorption of NO_X is accompanied by fast chemical reaction in the liquid phase and it is the gas-liquid contacting and mass transfer that usually need to be addressed to boost the overall absorption rate.

The mass transfer rate r from the gaseous into the liquid phase is given by

$$r = k\,a\,(C_i - C), \qquad kg/m^3 s \qquad (1)$$

where k is the overall mass transfer coefficient, m/s, a is the specific interfacial (the bubbles' surface per volume of liquid) area, m^{-1} and C_i is the concentration of dissolved gas at the bubble interface on the liquid side, kg/m^3.

The overall resistance $1/k$ to mass transfer is a sum of the resistance $1/k_G = \delta_G/D_G$ inside the gas bubble and the resistance $1/k_L = \delta_L/D_L$ across the diffusion film δ_L outside the bubble. Since diffusion coefficients D_G in gases are three to four orders of magnitude greater than D_L in liquids, the inside resistance is routinely ignored as negligible, $C_i \approx C^*$ which is the gas solubility given by the Henry's law and $C \approx 0$. The mass transfer is, therefore, controlled on the liquid side through the liquid film mass transfer coefficient k_L. Eq. (1) becomes

$$r \approx k_L \, a \, C^* \tag{2}$$

Numerous experimental data (cf. Calderbank (1959)) [5] for agitated vessels indicate that k_L is a function of liquid phase diffusivity D_L and not of power input or gas rate and diffusivities of gases in water or aqueous solutions do not vary much. Most, including those of oxygen and nitrogen oxide, are within $D_L = 1.8 \times 10^{-9}$—2.5×10^{-9} m^2/s range at room temperature [6]. Therefore, k_L is neither a scale-up variable, nor is it a factor affected by switching from oxygen to nitrogen oxide absorption. Furthermore, the solubility of oxygen and nitrogen oxide in water are also similar (e.g., $C^* = 35$ g/m^3 and 32 g/m^3 respectively at partial pressure of one atm and 50°C [6-7]) and do not change on scale-up which leaves the interfacial area a in Eq. (2) as the only variable to be addressed in scale-up.

In his review of published data on scale-up for gas sparged mechanically agitated tanks with geometric similarity and constant gas/liquid volume ratio, Hughmark (1980) [8] concluded that the interfacial area a was a function of a product $N^a D^b$, (or the impeller tip speed since a and b appeared to be close to unity) whose constancy preserves the constant gas-liquid mass transfer rate on scale-up. This scale-up rule does not necessarily address a separate issue of conversion which can be important whenever full utilization of pure gas (e.g., oxygen) or high scrubbing efficiency of harmful gas (e.g., NO$_X$) is required. In fact the rule is only accurate as long as gas bubbles are not noticeably depleted of the reactant consumed in the liquid phase which puts a limit on the reactant utilization and, ultimately, on a tank height. As long as the gaseous reagent, e.g., oxygen in the air used in waste water treatment or in aerobic fermentation, is inexpensive or harmless such "wasteful" practice is acceptable and even encouraged since it yields higher overall process rates. The approach must be different when pure oxygen is used or the gas is harmful. For example, very tall columns are employed to scrub NO$_X$ from off-gases even though mass transfer would have been much higher in gas sparged mechanically agitated tanks. The reason is low conversion of sparingly soluble gases per pass in the agitated tanks.

Self-aerated contactors, solve this dilemma and combine the best of mechanically agitated tanks and tall columns by recycling gas internally. As a function of the rotor tip speed or ND, the circulation rate Q_C, unlike the gas throughput Q_T, is not an independent parameter. Their ratio $F_c = Q_C/Q_T$, the circulation factor, serves as an equivalent of the column height assuring a specified conversion. Combined with ND, it can serve as a basis for the process scale-up where both, the

rates and the conversions are the parameters to be preserved. The constancy of the product $I = NDF_C$, the aeration index, assures the same conversion efficiency E on scale-up. It has been decided to devise a common scale-up procedure based on the data already obtained.

The scale-up Procedure
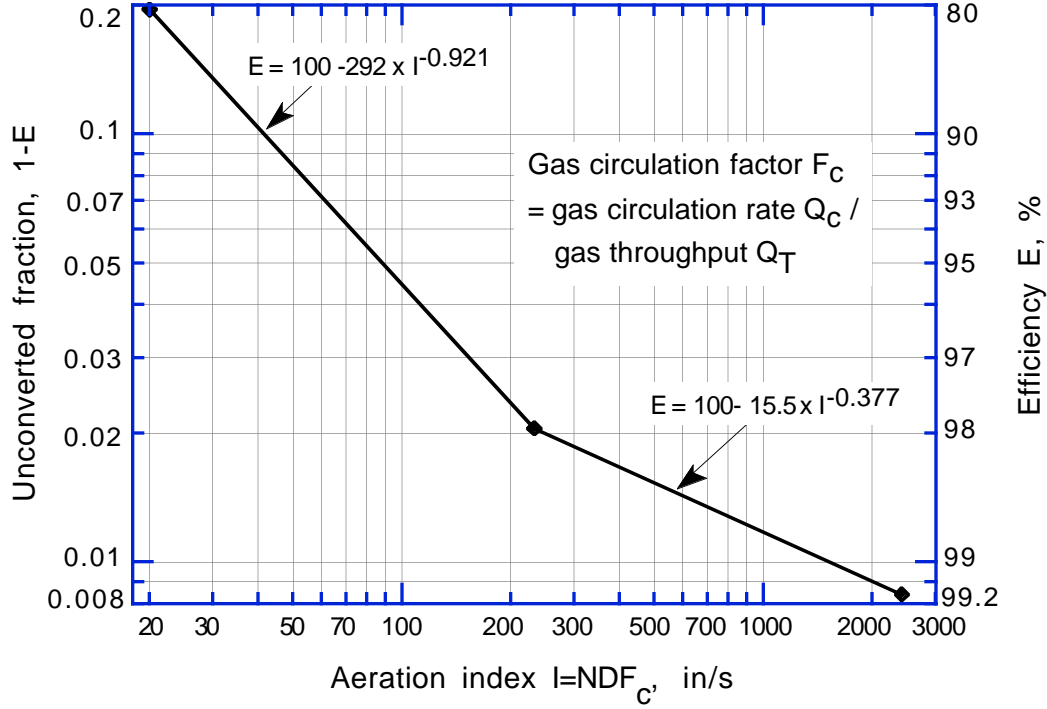
Fig. 1. Conversion efficiency as a function of aeration index

The fist step of the scale-up procedure is depicted in Fig. 1 where the aeration index I can be determined as soon as the conversion efficiency E is specified. Strong effect of mass transfer extending up to 98% conversion can be described by the relationship:

$$E = 100 - 292I^{-0.921} \tag{3}$$

As the reaction in liquid phase depleted of nitrous acid slows, the response to oxygen delivery weakens and the part of the curve corresponding to high conversion can be described by

$$E = 100 - 15.5I^{-0.377} \tag{4}$$

Note that the index I is dimensional and care must be taken to keep the units consistent throughout the scale-up. The plot in Fig. 1 was obtained from the results of MEO experiments (see also the Appendix A) where nitrous acid generated within the catholyte was oxidized back into nitric acid with pure oxygen fed into the contactor:

$$2HNO_2 + O_2 \rightarrow 2HNO_3 \tag{5}$$

4

Table 1. MEO Experimental Results

N	$[NO_x^{out}]$	Q_{O2}^{in}	E	Q_{O2}^{con}	Q_{O2}^{out}	Q_{NOx}^{out}	Q_T	Q_c	$F_c Q_c / Q_T$	$I = NDF_c$
s^{-1}	%	L/min	%	L/min	L/min	L/min	L/min	L/min	——	in/s
10	46.0	11.05	80.50	7.04	4.01	3.41	10.94	5.90	0.539	18.87
12	10.5	11.60	97.97	8.57	3.03	0.36	7.67	40.16	5.237	220.0
35	4.0	12.20	99.16	8.68	3.52	0.15	8.01	149.14	18.62	2281.0

The conversion efficiency E was defined twice, as a fraction of converted nitrous acid and as a ratio of oxygen consumed to that stoichiometrically required to oxidize all generated nitrous acid. As a function of current, the nitrous acid generation rate is well defined. Hence the maximum possible NO_X flow rate (if all nitrous acid became NO_X in the absence of conversion) was calculated as $Q_{NOx}^{max} = (I \cdot A)/2F$ from the current I, the Faraday number F, and the Avogadro number A. At I=2000 amp the electrochemical cell generated 13.9 standard liters of NO_X per minute corresponding to $Q_{NOx}^{max} = 17.5$ L/min at 70˚C, the temperature of MEO experiments. Similarly, the oxygen feed rate Q_{O2}^{in} is shown in Table 1 for 70˚C. The efficiency E was calculated from the expression (10A) obtained by Z. Chiba:

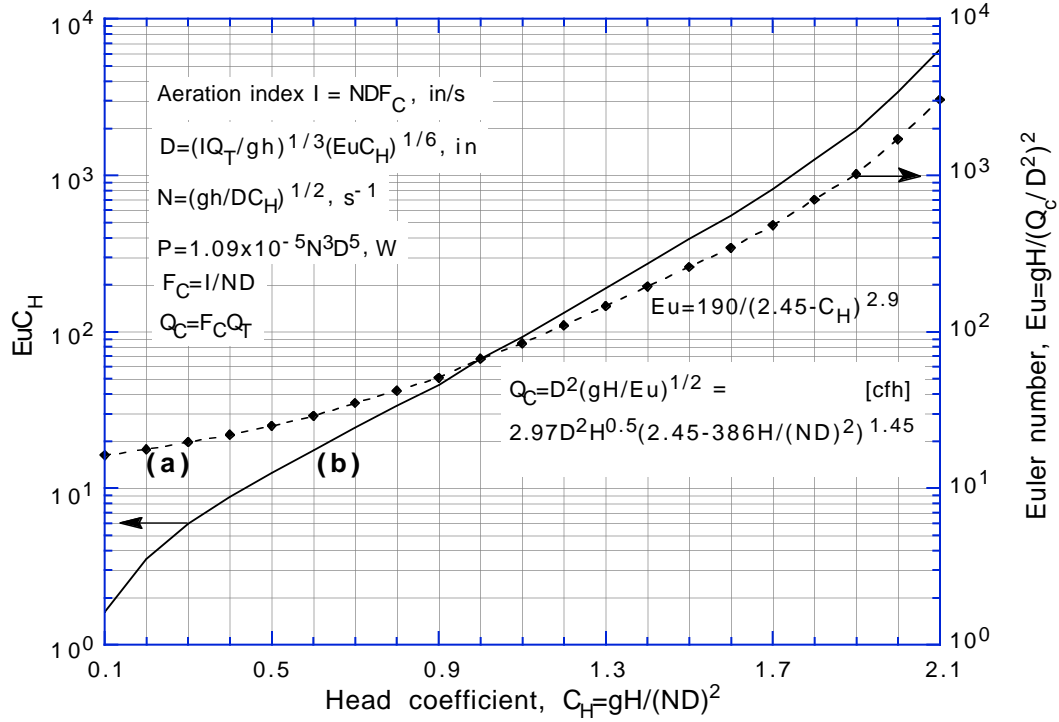$$E = \frac{1 - [NO_x^{out}]\left(1 + \dfrac{Q_{O2}^{in}}{Q_{NOx}^{max}}\right)}{1 - 1.5[NO_x^{out}]} , \tag{10A}$$

where the NO_X concentration $[NO_x^{out}]$ in the off-gas leaving the contactor and the oxygen flow rate Q_{O2}^{in} entering the contactor were measured. More detail on the experiments and the full derivation of (10A) are given in Appendix A. Equations (5A), (7A) and (8A) in the Appendix were used to calculate respectively Q_{NOx}^{out}, Q_{O2}^{out} and Q_{O2}^{con} in Table 1. For the average gas throughput Q_T across the converter the expression below was employed:

$$Q_T = \frac{Q_{O2}^{in} + Q_{O2}^{out}}{2} + Q_{NOx}^{out} \tag{6}$$

The second step of the scale-up procedure is associated with Fig. 2 adopted from the earlier publication by Zundelevich (1979) [4]. It represents generalization of experimental data on gas circulation capacity of variable size geometrically similar aerators (see Fig. 1B) expressed in terms of two dimensionless groups, the Euler number Eu and the rotor head coefficient C_H. All that is required to use Fig. 2 is the aeration index I (obtained from Fig. 1 once the conversion efficiency E is specified), the off-gas throughput Q_T across the contactor, and the dimensionless submergence $h = H/D$ (which also provides a convenient way to maintain the relationship between the aerator and the contactor sizes on scale-up). By selecting C_H from an approximate interval of 0.3 to 0.9, where operation is most economical, Eu and EuC_H are obtained and used

5

to determine the aerator rotor diameter D, the rotation speed N, the required power input P and the gas circulation rate Q_C. A detailed explanation of the above scale-up procedure can be found in Appendix B. A few examples of predicted gas circulation capacity are shown in Fig.3.

Inside the figure:

Aeration index $I = NDF_C$, in/s

$D = (IQ_T/gh)^{1/3}(EuC_H)^{1/6}$, in

$N = (gh/DC_H)^{1/2}$, s^{-1}

$P = 1.09 \times 10^{-5} N^3 D^5$, W

$F_C = I/ND$

$Q_C = F_C Q_T$

$Eu = 190/(2.45-C_H)^{2.9}$

(a)   (b)

$Q_C = D^2(gH/Eu)^{1/2} = \qquad$ [cfh]

$2.97 D^2 H^{0.5}(2.45-386H/(ND)^2)^{1.45}$

Left axis: EuC_H

Right axis: Euler number, $Eu = gH/(Q_c/D^2)^2$

X-axis: Head coefficient, $C_H = gH/(ND)^2$

Fig. 2. Dimensionless performance characteristics of turbo-aerator (a)-Experimental data plotted as Eu vs. C_H [4]; (b)-EuC_H vs. C_H

Inside the figure:

D=7" H=13"

$Q_C = 2.97 D^2 H^{0.5}(2.45-386H/(ND)^2)^{1.45}$

D=5" H=10"

D=3.5" H=7" (existing)

Y-axis: Gas circulation rate Q_C, SCFH

X-axis: Rotor speed N, Hz
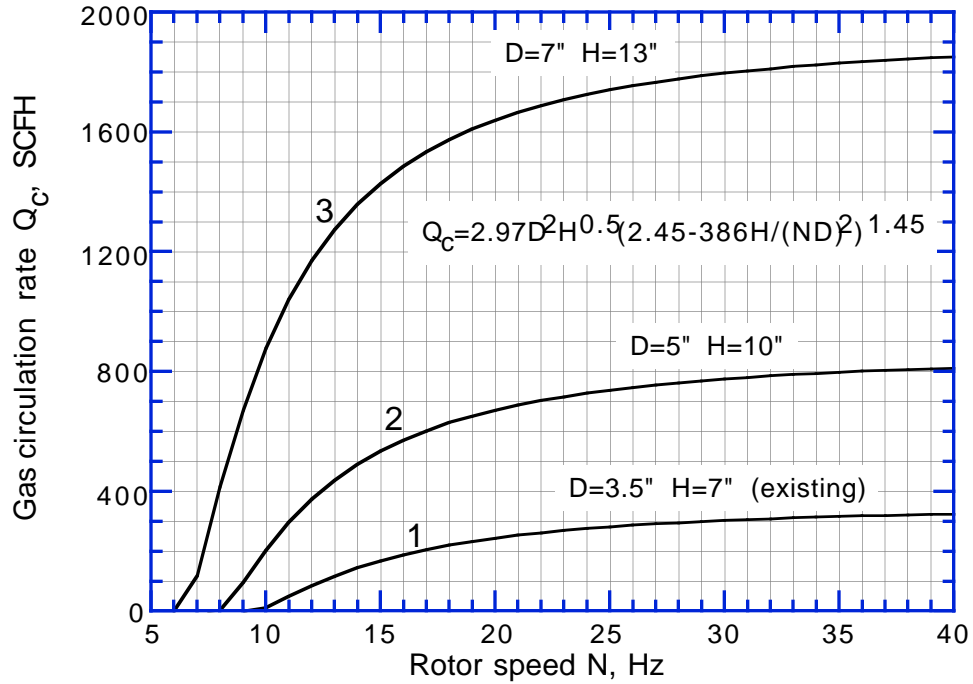
Fig. 3 Variation of gas circulation rate Q_C on scale-up

6

Scale-up of gas-liquid contactor for acidic urea DeNO$_X$

MWMF System Design Requirements for the Experimental Off-Gas Treatment call for a system capable of handling up to 10 m^3 of off-gas per hour. Assuming conversion efficiency of 98.5% and the geometry similar to the existing bench-scale converter, the following design steps can be accomplished using only Figs. 1 and 2.

<u>Given:</u> Q_T = 10 m^3/h = 353 cfh = 170 in^3/s, E = 98.5%, h =1.9

Step 1. From Fig.1: $I = NDF_C$ = 600 in/s

Step 2. From Fig.2: for C$_H$ =0.3 Eu = 20 and EuC$_H$ = 6.

    Using equations (14B) and (15B) shown in Fig. 2 obtain: D = 6.98", N = 18.7 s^{-1}.

    Use standard motor with 1140 rpm = 19 Hz and D = 7"

    Using equation (8B), power input: P = 1.09x10^{-5} N^3D^5 = 1.09x10^{-5} 19^{3}7^5 = 1258 W

    F_C = I/ND = 600/(19x7) = 4.51

    Q_C = 353·4.51= 1592 cfh

    From Fig.3 (curve 3): maximum Q_C =1610 cfh at N = 19 Hz.

Step 3. Aerator submergence $H = hD$ = 1.9x7 = 13". By setting the distance to the tank bottom equal to the aerator rotor diameter 7", the total liquid fill height 13"+7"=20". Select tank diameter T = 22" and the tank height H_T = 33".

Note, that from the power consumption standpoint the optimum design would have required C$_H$ =0.9 [4] (see also Appendix B). Proceeding with this option:

Step 2. From Fig.2: for C$_H$ =0.9 Eu = 53 and EuC$_H$ = 48.

    Using equations in Fig. 2 obtain: D = 9.86", N = 9.1 s^{-1} = 545 rpm.

    Power input: P = 1.0913x10^{-5} N^3D^5 = 1.0913x10^{-5} 9.1^{3}x9.86^5 = 764 W

    F_C = I/ND = 600/(9.1x9.87) = 6.7

    Q_C = 353x6.7 = 2362 cfh

    Since there is no small motors with 545 rpm, a gear box would be required.

Step 3. Aerator submergence $H = hD$ = 1.9x9.86 = 18.75". By setting the distance to the tank bottom equal to the aerator rotor diameter 9.86", the total liquid fill height 18.75"+9.86"=28.6". The resulting tank diameter T = 30" and the tank height H_T = 45".

With a simple FORTRAN code (given in Appendix C) performing essentially the same steps, a table of design options like the one below can be generated and reviewed.

    PROGRAM AERATOR SCALE-UP

    Gas Throughput Q_T = 353.0 cfh
    Dimensionless Submergence $h=H/D$ = 1.90

C_H	V_{liq}	N	Q_C	T	H_T	F_c	D	P
--	liter	rpm	cfh	in	in	--	in	W

Aeration Index $I = 300.0$ in/s   Efficiency $E = 98.14$ %

C_H	V_{liq}	N	Q_C	T	H_T	F_c	D	P
0.2	48.8	1610.9	775.2	16.0	24.0	2.20	5.09	719.6
0.3	63.8	1257.7	907.8	17.5	26.3	2.57	5.57	535.9
0.4	79.0	1051.2	1011.7	18.8	28.2	2.87	5.97	446.2
0.5	94.9	911.8	1096.9	20.0	30.0	3.11	6.35	395.8
0.6	112.2	809.5	1168.6	21.2	31.7	3.31	6.72	366.0
0.7	131.4	730.0	1229.5	22.3	33.5	3.48	7.08	349.1
0.8	153.0	665.8	1281.4	23.5	35.2	3.63	7.45	341.2
0.9	177.7	612.2	1325.7	24.7	37.0	3.76	7.83	340.5

Aeration Index $I = 600.0$ in/s   Efficiency $E = 98.57$ %

C_H	V_{liq}	N	Q_C	T	H_T	F_c	D	P
0.2	97.6	1435.2	1381.2	20.2	30.3	3.91	6.41	1615.3
0.3	127.6	1120.5	1617.6	22.1	33.1	4.58	7.01	1202.9
0.4	157.9	936.6	1802.7	23.7	35.6	5.11	7.53	1001.6
0.5	189.9	812.4	1954.6	25.2	37.8	5.54	8.00	888.4
0.6	224.5	721.2	2082.2	26.7	40.0	5.90	8.46	821.7
0.7	262.8	650.4	2190.7	28.1	42.1	6.21	8.92	783.7
0.8	306.0	593.1	2283.3	29.6	44.3	6.47	9.38	766.0
0.9	355.3	545.4	2362.2	31.1	46.6	6.69	9.86	764.3

Aeration Index $I = 1200.0$ in/s   Efficiency $E = 98.90$ %

C_H	V_{liq}	N	Q_C	T	H_T	F_c	D	P
0.2	195.1	1278.6	2461.1	25.4	38.2	6.97	8.08	3625.9
0.3	255.3	998.3	2882.2	27.8	41.7	8.16	8.83	2700.2
0.4	315.8	834.4	3212.0	29.9	44.8	9.10	9.48	2248.4
0.5	379.7	723.8	3482.7	31.8	47.6	9.87	10.08	1994.2
0.6	448.9	642.5	3710.0	33.6	50.4	10.51	10.66	1844.5
0.7	525.6	579.4	3903.4	35.4	53.1	11.06	11.24	1759.3
0.8	611.9	528.4	4068.4	37.2	55.9	11.53	11.82	1719.5
0.9	710.6	485.9	4209.0	39.1	58.7	11.92	12.43	1715.7

Compared to the actually selected design (at $C_H = 0.3$), the "optimum" version at $C_H = 0.9$ saves power but requires motor gear and increases tank volume (to accommodate larger aerator without wall effects) which is hardly justified on a small scale. However, optimum design would be a logical choice for large and deep commercial units consuming tens or hundreds of kilowatts of power. As the scale (and the submergence) keeps increasing, a point is usually reached where a cascade of smaller tanks becomes economically preferable to a single large and deep unit.

Scale-up of gas-liquid contactor for MEO nitrous acid converter

MWMF System Design Requirements for Mediated Electrochemical Oxidation call for 12,500 A integrated cell current, a scale factor of 6.25 over the present 2,000 A. The average gas throughput Q_T can be estimated, as before, with the expression (6). For I = 12,000 A $Q_{O2}^{sto} = 1/2 Q_{NOx}^{max} = (I \cdot A)/4F = 44.2$ L/min (stp) or 54.7 L/min at 70˚C. Assuming conversion

efficiency of 98.5% and 30% excess oxygen (for the sake of Q_T estimate), we obtain $Q_{O2}^{con} = EQ_{O2}^{sto} = 53.9$ L/min, $Q_{NOx}^{out} = (1-E)Q_{NOx}^{max} = 1.6$ L/min and $Q_{O2}^{in} = 53.9 \times 1.3 = 70$ L/min. Then from (6):

$$Q_T = \frac{Q_{O2}^{in} + Q_{O2}^{out}}{2} + Q_{NOx}^{out} = \frac{70 + 16.1}{2} + 1.6 = 44.7 \ \text{L/min}$$

Assuming $Q_T = 45$ L/min $= 95.3$ cfh and the geometry similar to the existing bench-scale converter, the following design options can be generated and reviewed.

Gas Throughput $Q_T = 95.3$ cfh
Dimensionless Submergence $h = H/D = 1.90$

C_H	V_{liq}	N	Q_C	T	H_T	F_c	D	P
--	liter	rpm	cfh	in	in	--	in	W

Aeration Index $I = 300.0$ in/s   Efficiency $E = 98.14$ %

C_H	V_{liq}	N	Q_C	T	H_T	F_c	D	P
0.2	13.2	2003.8	260.3	10.4	15.5	2.73	3.29	156.2
0.3	17.2	1564.4	304.8	11.3	17.0	3.20	3.60	116.3
0.4	21.3	1307.6	339.7	12.2	18.2	3.56	3.86	96.9
0.5	25.6	1134.2	368.4	12.9	19.4	3.87	4.11	85.9
0.6	30.3	1006.9	392.4	13.7	20.5	4.12	4.34	79.5
0.7	35.5	908.0	412.9	14.4	21.6	4.33	4.58	75.8
0.8	41.3	828.1	430.3	15.2	22.7	4.52	4.81	74.1
0.9	48.0	761.5	445.2	15.9	23.9	4.67	5.06	73.9

Aeration Index $I = 600.0$ in/s   Efficiency $E = 98.57$ %

C_H	V_{liq}	N	Q_C	T	H_T	F_c	D	P
0.2	26.3	1785.2	463.8	13.1	19.6	4.87	4.14	350.6
0.3	34.5	1393.8	543.2	14.3	21.4	5.70	4.53	261.1
0.4	42.6	1164.9	605.3	15.3	23.0	6.35	4.86	217.4
0.5	51.3	1010.5	656.4	16.3	24.4	6.89	5.17	192.8
0.6	60.6	897.0	699.2	17.2	25.8	7.34	5.47	178.4
0.7	71.0	809.0	735.6	18.2	27.2	7.72	5.77	170.1
0.8	82.6	737.8	766.7	19.1	28.7	8.05	6.06	166.3
0.9	95.9	678.5	793.2	20.1	30.1	8.32	6.37	165.9

Aeration Index $I = 1200.0$ in/s   Efficiency $E = 98.90$ %

C_H	V_{liq}	N	Q_C	T	H_T	F_c	D	P
0.2	52.7	1590.4	826.4	16.4	24.7	8.67	5.22	787.1
0.3	68.9	1241.7	967.9	18.0	27.0	10.16	5.71	586.1
0.4	85.3	1037.9	1078.6	19.3	29.0	11.32	6.13	488.1
0.5	102.5	900.2	1169.5	20.5	30.8	12.27	6.52	432.9
0.6	121.2	799.2	1245.9	21.7	32.6	13.07	6.89	400.4
0.7	141.9	720.7	1310.8	22.9	34.3	13.75	7.26	381.9
0.8	165.2	657.3	1366.2	24.1	36.1	14.34	7.64	373.3
0.9	191.9	604.4	1413.4	25.3	37.9	14.83	8.03	372.4

Since it is very desirable to reduce the overall nitric acid inventory in the MEO system, there is a strong incentive to keep V_{liq} and, therefore, the contactor size at a minimum. Given the low gas throughput, that is easily done, indicating that the MEO contactor is going to be much smaller

then the acidic urea DeNO$_X$ contactor. Thus the earlier arguments favoring low C$_H$ for small scale remain applicable. A suitable design, among the above options, can be located in the vicinity of the lines:

C$_H$	V_{liq}	N	Q_C	T	H_T	Fc	D	P
--	liter	rpm	cfh	in	in	--	in	W
0.2	26.3	1785.2	463.8	13.1	19.6	4.87	4.14	350.6
0.3	34.5	1393.8	543.2	14.3	21.4	5.70	4.53	261.1

By selecting $D = 4.5"$, $H = 9"$, $T = 14"$, $H_T = 21"$ and $N = 28.75$ s^{-1} = 1725 rpm (using standard motor), the maximum power consumption $P = 1.0913 \times 10^{-5} N^3 D^5 = 1.0913 \times 10^{-5}$ $28.75^3 \times 4.5^5 = 478$ W. Hence 0.75 hp motor would be adequate. From Eq. (5B) the maximum gas circulation rate $Q_C = 582$ cfh, $Fc = 582/95.3 = 6.1$ and the aeration index $I = 6.1 \times 4.5 \times 28.75 = 789$ in/s. From Eq. (4) the maximum efficiency $E = 98.75\%$. Comparing $V_{liq} = 35$ L for this unit with $V_{liq} = 20$ L in the existing unit it can be concluded that the adequate converter for 2,000 A cell could have been made considerably smaller.

Appendix A. Calculation of nitrous acid conversion efficiency from the results of the MEO experiments

On the cathode side of the MEO cell the electrolyte ($\approx$6 molar nitric acid) is reduced to nitrous acid via the reaction:

$$HNO_3 + 2e^- + 2H^+ \rightarrow HNO_2 + H_2O \tag{1A}$$
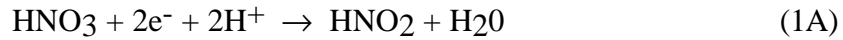
If the nitrous acid is allowed to build up, it will decompose via the reaction:

$$HNO_2 \rightarrow 1/2NO_2 + 1/2NO + 1/2H_2O \tag{2A}$$
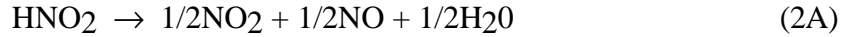
Besides producing large amount of NO$_X$ (one mole of HNO$_2$ produces one mole of NO$_X$ as an equimolar mixture of NO$_2$ and NO), this also causes net nitric acid loss to the system and could trigger generation of hydrogen at the cathode once the nitric acid concentration drops below about 2 molar.

To prevent all of the above from happening, the catholyte is continually circulated through the Nitrous Acid Converter, as shown in Fig. 1A, where the nitrous acid is oxidized back into nitric via the reaction:

$$HNO_2 + 1/2O_2 \rightarrow HNO_3 \tag{3A}$$

10
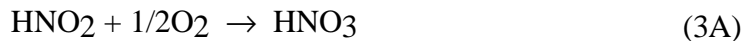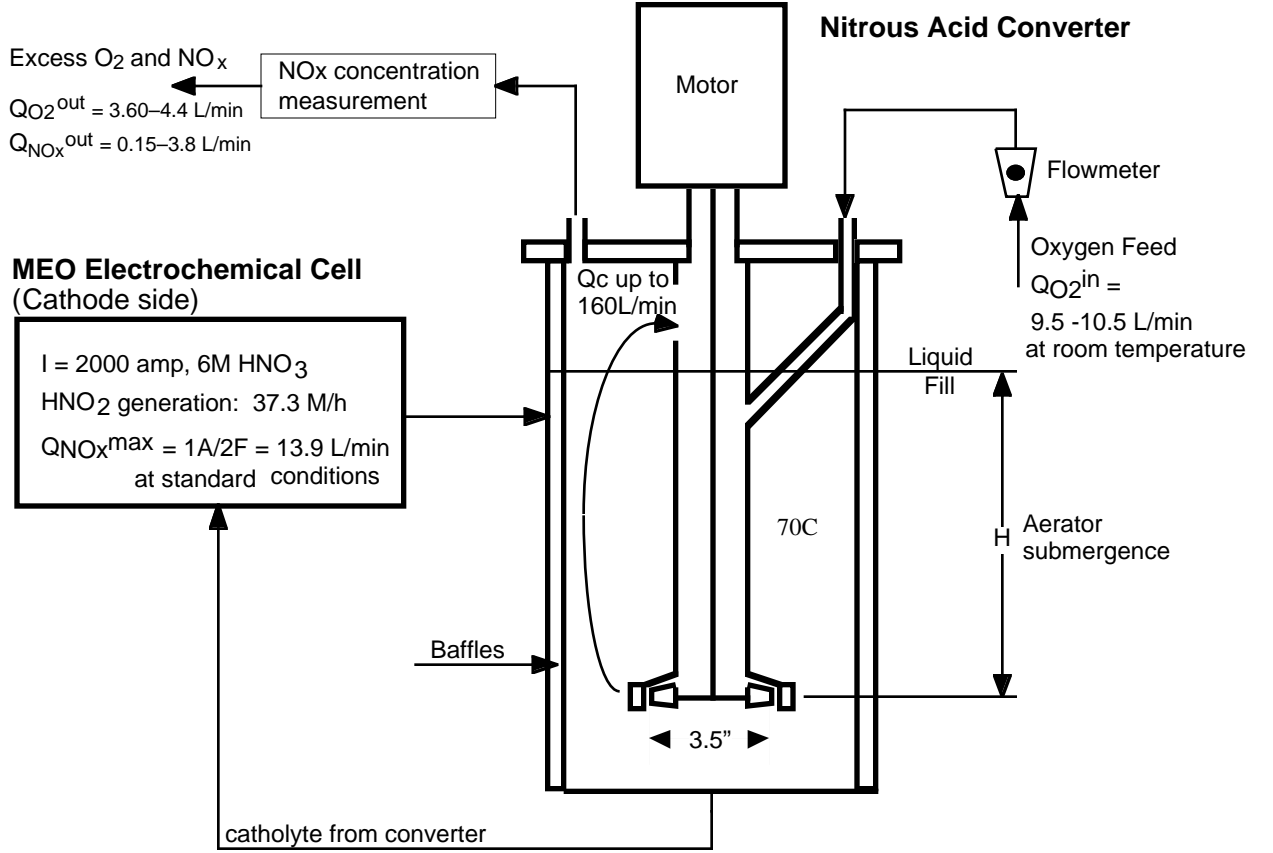
Fig. 1A. Nitrous acid conversion experiment schematic

The Nitrous Acid Converter is the gas-liquid contactor described earlier, into which oxygen is fed at ambient pressure and temperature. The oxygen feed rate Q_{O2}^{in}, measured by the flow meter, is kept slightly above Q_{O2}^{sto}, the stoichiometric oxygen requirement for complete oxidation of all nitrous acid being generated. As a function of the sell current I, the nitrous acid generation rate is fully predictable and so is its NO_x equivalent Q_{NOx}^{max}, the maximum NO_x generation rate in the absence of HNO_3 regeneration:

$$Q_{NOx}^{max} = (IA)/2F , \qquad (4A)$$

where A = 22.4 L/mole is Avogadro number and F = 96500 coulomb/mole is Faraday number. The conversion efficiency E was defined two ways, as a fraction of converted nitrous acid (potential NO_x) and as a ratio of consumed oxygen Q_{O2}^{con} to that stoichiometrically required to oxidize all nitrous acid:

$$E = 1 - \frac{Q_{NOx}^{out}}{Q_{NOx}^{max}} = \frac{Q_{O2}^{con}}{Q_{O2}^{sto}} \qquad (5A)$$

The unknown quantity Q_{NOx}^{out} in (5A), the rate of unconverted NO_x release, can be expressed through its measured concentration $[NO_x^{out}]$ in a mixture of unconverted NO_x and the unused oxygen which constitutes the complete MEO off-gas on the cathode side:

11

$$Q_{NO_x}{}^{out} = [NO_x{}^{out}](Q_{NO_x}{}^{out} + Q_{O2}{}^{out}) \qquad (6A)$$

Defining the rate of release of unused oxygen in (6A) as
$$Q_{O2}{}^{out} = Q_{O2}{}^{in} - Q_{O2}{}^{con}, \qquad (7A)$$

and expressing $Q_{O2}{}^{con}$ in (7A) through (5A) and the stoichiometric relationship $Q_{O2}{}^{sto} = 1/2Q_{NO_x}{}^{max}$
$$Q_{O2}{}^{con} = EQ_{O2}{}^{sto} = 1/2EQ_{NO_x}{}^{max}, \qquad (8A)$$
we have from (6A-8A) for $Q_{NO_x}{}^{out}$:

$$Q_{NO_x}{}^{out} = \frac{Q_{O2}{}^{out}[NO_x{}^{out}]}{1-[NO_x{}^{out}]} = \frac{(Q_{O2}{}^{in} - 0.5EQ_{NO_x}{}^{max})[NO_x{}^{out}]}{1-[NO_x{}^{out}]}. \qquad (9A)$$

Substituting (9A) into (5A)
$$E = 1 - \frac{(Q_{O2}{}^{in} - 0.5EQ_{NO_x}{}^{max})[NO_x{}^{out}]}{(1-[NO_x{}^{out}])Q_{NO_x}{}^{max}},$$

and solving for E, the expression (10A) used to calculate nitrous acid conversion efficiency during MEO experiments is obtained:

$$E = \frac{1-[NO_x{}^{out}]\left(1 + \dfrac{Q_{O2}{}^{in}}{Q_{NO_x}{}^{max}}\right)}{1-1.5[NO_x{}^{out}]} \qquad (10A)$$

Appendix B. Development of the scale-up procedure for self-inducting turbo aerators

As a part of theoretical and experimental investigation of self-inducting turbo aerator performance, Y. Zundelevich (1979) [4], demonstrated a unique relationship between two dimensionless groups, the Euler number
$$\text{Eu} = \frac{gH}{(Q_c/D^2)^2} \qquad (1B)$$
and the head coefficient
$$C_H = \frac{gH}{(ND)^2}, \qquad (2B)$$
which laid out a basis for the scale-up of geometrically similar aerators. He also formed optimality criterion Q_cH/P [4] from the key aerator characteristics such as its gas inducing capacity Q_c and the power consumption P at a given submergence H and showed that within practically important C_H range where Q_cH/P was high, it was another unique function of C_H. The design of the aerator (see Fig. 1B) intended for nitrous acid conversion and for acidic urea

DeNO$_X$ was perfected earlier [3, 4] on the basis of the above criterion which attains maximum value of $Q_cH/P = 0.039 \frac{\text{m}^4}{\text{Wh}} = 4.5 \frac{\text{ft}^4}{\text{Wh}}$ at C$_H$ = 0.9.
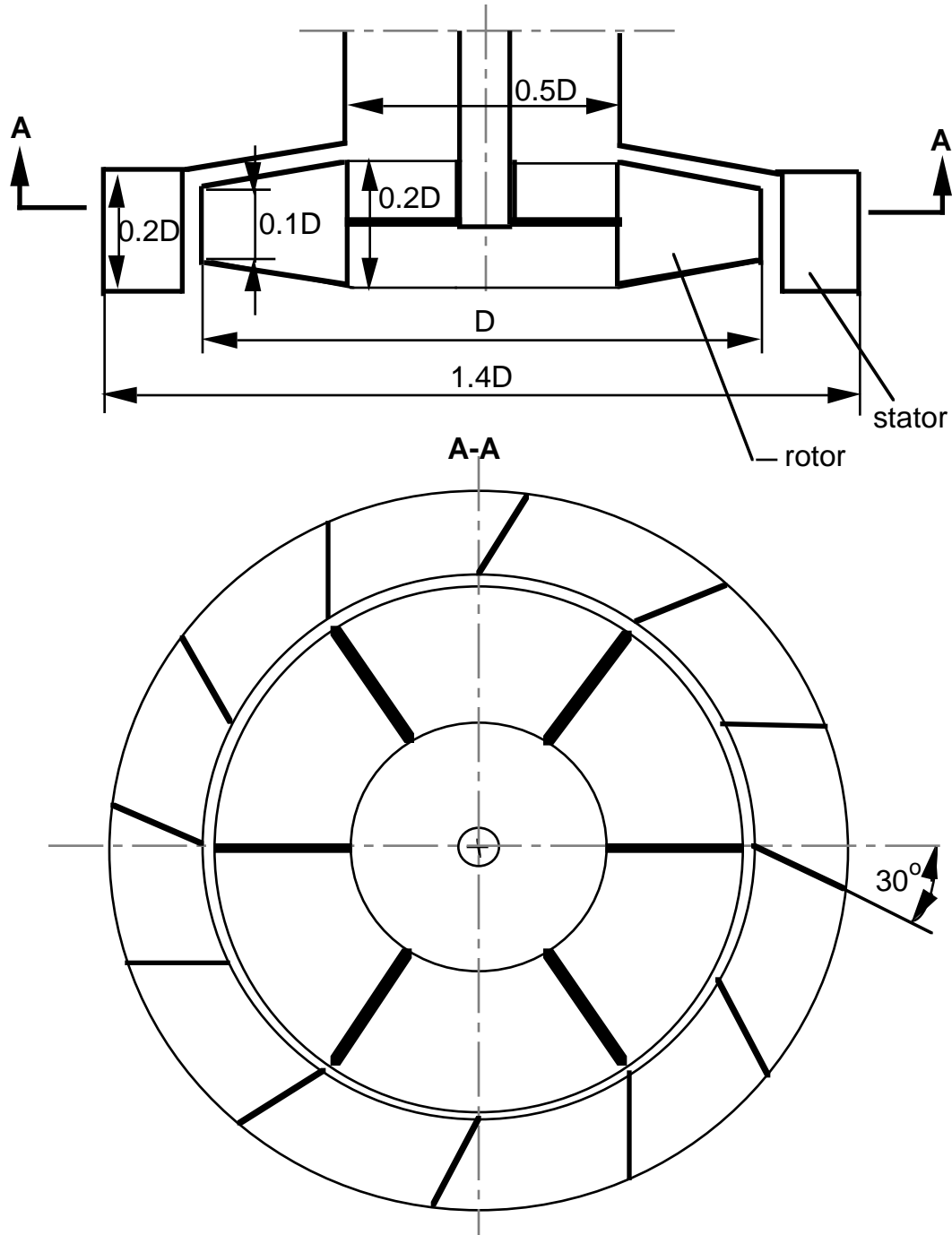
Fig. 1B. Turbo aerator geometry

 The Eu – C$_H$ relationship for this design, based on the experiments with three aerator diameters D and covering broad ranges of rotational speed N and submergence H [4], is shown in Fig. 2 together with its analytical expression:

$$Eu = \frac{190}{(2.45 - C_H)^{2.9}} \qquad (3B)$$

It relates the main aerator characteristic, its gas inducing capacity Q_c, to the three primary operational/design parameters D, N and H. Solving (1B) for Q_c

$$Q_c = D^2 \sqrt{\frac{gH}{Eu}} \qquad (4B)$$

or substituting (3B) into (4B)

$$Q_c = 2.97 D^2 \sqrt{H} \left(2.45 - \frac{386H}{(ND)^2} \right)^{1.45}, \qquad (5B)$$

two equivalent equations predicting the gas inducing capacity Q_c are obtained. In Eq. (4B) any consistent units can be used. Eq. (5B) yields Q_c in cfh when D and H are in inches and N is in Hz (see example in Fig. 3).

A typical design procedure begins with the selection of C_H from an interval of 0.3 to 0.9. The lower numbers, despite less then ideal use of power, tend to simplify the design on a small scale dominated by low submergence and high speed motors. The power efficiency, however, does become important for larger, deeper units and $C_H = 0.9$ corresponding to the maximum $Q_c H/P = 4.5 \frac{ft^4}{Wh}$ should be used to obtain the most economical solution.

When the aerator gas circulation rate Q_c and the submergence H are specified, the required power input P at $C_H = 0.9$ follows directly from $Q_c H/P = 4.5 \frac{ft^4}{Wh}$ (for C_H other then 0.9 a plot of $Q_c H/P$ vs. C_H [4] can be used). The aerator rotor diameter is determined by solving (1B) for D

$$D = \sqrt[4]{\frac{Q_c^2 Eu}{gH}}, \qquad (6B)$$

with the value for Eu given by (3B) or taken from Fig. 2. Finally, the aerator rotational speed is determined by solving (2B) for N using the above value for D :

$$N = \sqrt{\frac{gH}{D^2 C_H}} \qquad (7B)$$

For $C_H \leq 0.9$, P can be also calculated from

$$P = 1.09 \times 10^{-5} N^3 D^5, \quad W \qquad (8B)$$

where D is in inches and N is in Hz.

When, instead of the circulation rate Q_c, the off-gas throughput rate Q_T and the conversion efficiency E are specified, as in the case of gas-liquid absorption accompanied by chemical reaction, the aeration index $I = NDF_c$ necessary to achieve that efficiency would have to be located on the plot of Fig. 1 in addition to selecting C_H, as the first step. From the performance and the economics points of view respectively, both parameters have profound effect on the

aerator design and will, therefore, feature prominently throughout the scale-up procedure. Using the definitions of the circulation factor and the aeration index

$$F_c = \frac{Q_c}{Q_T} = \frac{I}{ND}, \quad (9B)$$

the required circulation rate can be expressed in terms of the off-gas throughput and the aeration index:

$$Q_c = Q_T \frac{I}{ND} \qquad (10B)$$

Substitution of (2B) solved for $(ND)^2$ into (10B) squared, expresses it in terms of C_H

$$Q_c^2 = Q_T^2 \frac{I^2 C_H}{gH} \qquad (11B)$$

Substitution of (11B) into (6B) leads to the aerator rotor diameter expressed in terms of the design parameters of interest:

$$D = \sqrt[4]{\frac{I^2 Q_T^2 EuC_H}{(gH)^2}} = \sqrt{\frac{IQ_T}{gH}} \, (EuC_H)^{1/4} \qquad (12B)$$

The aerator rotational speed N is given by (7B) for the above value of D. Using (9B), the circulation factor F_c corresponding to these N and D and the circulation rate Q_c can be calculated.

In the described procedure the aerator submergence H was treated as an independent parameter providing a degree of flexibility for selecting the aerator and the tank.

If proportionality between the aerator and the contactor geometry is to be preserved on scale-up, dimensionless submergence expressed in terms of the aerator rotor diameter can be used

$$h = H/D \qquad (13B)$$

Substitution of $H = hD$ into (12B) and (7B) yields expressions for D and N in terms of h:

$$D = \sqrt[3]{\frac{IQ_T}{gh}} \, (EuC_H)^{1/6} \qquad (14B)$$

and

$$N = \sqrt{\frac{gh}{DC_H}} \qquad (15B)$$

Any consistent units can be used in Eqs. (6B-15B). Note that I has a dimension "length/time" and is shown in "in/s" in Fig. 1.

Appendix C. Program for designing gas-liquid contactors with self-inducting turbo aerators

```
PROGRAM AERSCALEUP
   REAL*4 I,N
   LU=9
   g=386.1              !  acceleration of gravity, in/s2
   h=1.9                !  dimensionless submergence
```

```
      Qt=353                ! gas throughput, cfh
      I=300            ! aeration index, in/s
      WRITE(LU,'(9X,''PROGRAM AERATOR SCALE-UP'')')
      WRITE(LU,'(/9X,''Gas Throughput Qt, cfh ='',F6.1)') Qt
      WRITE(LU,'(9X,''Dimensionless Submergence h=H/D ='',F5.2)') h
      WRITE(LU,'(/'' CH     Vliquid       RPM         Qcirc       Tdiam
     1Theight   Fcirc     Drotor      Power'')')
      WRITE(LU,'('' --      liter        rpm           cfh          in
     1in       --       in          W'')')
  20  E=100.0-15.5*I**(-.377)  ! efficiency, %
      WRITE(LU,'(/9X,''Aeration Index I, in/s ='',F6.1)') I
      WRITE(LU,'(9X,''Efficiency E ='',F6.2)') E
      CH=.2
  10  Eu=190.0/(2.45-CH)**2.9
      D=((I*0.48*Qt)/(g*h))**.3333*(Eu*CH)**.16667 ! diam., in
      N=SQRT((g*h)/(D*CH))   ! rot. speed, 1/s
      RPM=60.0*N
      P=1.09e-5*N**3.0*D**5.0        !  power, W
      Fc=I/(N*D)    ! circulation factor
      Qc=Fc*Qt     !  gas circulation capacity, cfh
      T=3.15*D    ! tank diameter, in
      HL=D*(1.0+h)  !  liquid fill, in
      Ht=1.5*T     !  tank height, in
      VL=0.01287*T**2.0*HL   !  liquid volume, Liters
      WRITE(LU,25) CH,VL,RPM,Qc,T,Ht,Fc,D,P
  25  FORMAT(F3.1, F10.1, 2F11.1, 2F10.1, 2F10.2, f11.1)
      IF (CH.LE.0.9.AND.I.LE.1200.) THEN
      CH=CH+0.1
      GOTO 10
      ELSEIF (I.LT.1200.) THEN
      I=I+300.
      GOTO 20
      END IF
      read (5,*) iend
      STOP
      END
```

Nomenclature

a = specific interfacial (the bubbles' surface per volume of liquid) area, m^{-1}

A = 22.4 L/mole = Avogadro number

C^* = gas solubility in water or aqueous solutions, g/m^3

$C_H = \dfrac{gH}{(ND)^2}$ = head coefficient

D = aerator rotor diameter, m

D_L = gas diffusivity in liquid phase, m^2/s

E = conversion efficiency

$Eu = \dfrac{gH}{(Q_C/D^2)^2}$ = Euler number

$F_C = Q_C/Q_T$ = circulation factor

F = 96500 coulomb/mole = Faraday number

g = acceleration of gravity, m/s^2

H = aerator submergence, m

H_T = tank height, m

$I = NDF_C$, the aeration index, m/s

I = current, A

k_L = liquid film mass transfer coefficient, m/s

N = rotor rotational speed, rpm, s^{-1}

[NO$_X^{out}$] = unconverted NO$_X$ concentration in off-gas, %, ppm

P = power consumption, W

Q_C = gas circulation rate, m^3/s

Q_T = gas throughput, m^3/s

Q_{NOx}^{max} = (I·A)/2F = maximum possible NO$_X$ flow rate generated at the cathode, m^3/s

Q_{NOx}^{out} = rate of unconverted NO$_X$ release, m^3/s

Q_{O2}^{sto} = stoichiometric oxygen requirement for complete oxidation of nitrous acid, m^3/s

Q_{O2}^{in} = oxygen feed rate, m^3/s

Q_{O2}^{con} = oxygen consumption rate, m^3/s

r = mass transfer rate, kg/m^{3}s

T = tank diameter, m

V_{liq} = liquid volume in 2/3 filled tank, m^3

References

(1)   K. R. Jethani, N. J. Suchak and J. B. Joshi, Selection of Reactive Solvent For Pollution Abatement of NO$_X$, Gas Sep. Purif., **4**, 9, (1990)

(2)   A. Warshaw, Removal of Nitrogen Oxides From a Gas Stream - US Patent 3 565 575 (1971)

(3)   Y. Zundelevich and E. Vigdorchik, Applications of Self-Inducting Impellers in Autoclave Leaching, Proc. All-Union Conf. on Application of Autoclave Technology in Non-Ferrous Metallurgy, Moscow, (1975)

(4)   Y. Zundelevich, Power Consumption and Gas Capacity of Self-Inducting Turbo-Aerators, AIChE Journal, **25**, 763-773, (1979)

(5)   P. H. Calderbank, Physical Rate Processes in Industrial Fermentation, Part II: The Mass-Transfer Coefficients for Gas-Liquid Contacting in Agitated Vessels, Trans. Inst. Chem. Engrs., (London) **37**, 173 (1959)

(6)   Perry's Chemical Engineers' Handbook, 6th ed., p. 3-103, McGraw-Hill, New York, 1984

(7)   CRC Handbook of Chemistry and Physics, p. B-103, The Chemical Rubber Co., 1974

(8)   G. A. Hughmark, Power Requirements and Interfacial Area in Gas-Liquid Turbine Agitated Systems, Ind. Eng. Chem. Process Des. Dev., **19**, 638-641, (1980)

Technical Information Department • Lawrence Livermore National Laboratory
University of California • Livermore, California 94551